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CONTACT DERMATITIS

Methacrylates in dental restorative materials

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Commercial dental restorative materials were analysed in order to obtain information about the occurrence of sensitizing acrylates. Acetone-soluble methacrylates of 7 bonding materials, 8 composite resins and 2 glass ionomers were identified by gas chromatography with mass-selective detection and quantified by liquid chromatography with ultraviolet detection. The most frequently occurring methacrylates in the bonding materials were 2-hydroxyethyl methacrylate (2-HEMA) and 2,2-bis-[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane (bis-GMA). Bis-GMA and triethyleneglycol dimethacrylate were the most frequently occurring methacrylates in composite resins. The main methacrylate of the 2 glass ionomers was 2-HEMA or trimethylolpropane trimethacrylate. Information about methacrylates was given in the safety data sheets (SDSs) for about half of the products that according to the analysis results contained methacrylates. SDSs need to be improved so that the health risks for dental personnel can be reliably assessed and controlled.

Key words: 2-HEMA; bis-GMA; bonding materials; chromatography; composite resins; dental personnel; glass ionomers; methacrylates; occupational; safety assessment; TEGDMA. © Blackwell Munksgaard, 2004.

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Methacrylic compounds are nowadays widely used in restorative dentistry, as composite resin restorations have almost completely replaced amalgam fillings.

Allergic contact dermatitis is a well-known adverse health effect of methacrylates (1), but they also cause respiratory hypersensitivity including asthma (2). During 1975–98, 140 cases of allergic contact dermatitis and 18 cases of asthma were reported to the Finnish Register of Occupational Diseases. Most of the cases are from the 1990s by when the usage of plastic fillings had increased significantly (1, 2).

We have recently shown that dental personnel, both nurses and dentists, are exposed to small amounts of airborne methacrylates, mainly 2-hydroxyethyl methacrylate (2-HEMA) and triethyleneglycol dimethacrylate (TEGDMA), during the application of resin material as well as during the drilling work of composite resin restoratives (3). Dental clinics should get information about hazardous compounds in their restorative materials from the safety data sheets (SDSs), as in Finland the ministry of social affairs has enforced the European Union (EU) directive 1999/45/EC to apply to dental restorative materials (4).

The aim of the study was to identify the methacrylates and to determine their concentrations in commercial dental restorative materials, in order to obtain information about the occurrence of sensitizing methacrylates. The analytical results were compared to information given in the SDSs.

Materials and Methods

Product samples were acquired from the distributors (Table 1). The selected samples were representatives of dental restorative materials, both bonding materials and composite resins, commonly in use in Finland during 2001 and 2002.

The specimen was accurately weighed and dissolved in acetone to obtain concentrations of about 0.5 and 2 mg/ml for quantification. Concentrations of 2–10 mg/ml were used for identification. All solvents in use were of analytical reagent grade.

The identification was performed on a gas chromatograph (GC, Agilent 6890) equipped with autosampler and a mass-selective (MS, Agilent 5973N) detector. The column used for the separation was HP-5MS [30 m, 0.25 mm inner diameter (ID), 0.25 μm film thickness]. The injector was operated in the splitless mode and the injector temperature was 250°C. The GC was operated in the constant flow mode with an average velocity of 41 cm/s. The initial oven temperature of 40°C

Table 1. The products studied and their manufacturers

Product	Manufacturer
Bonding materials (adhesive resins and primers)	
Allbond 2 D/E bonding resin	Bisco Inc., Schamburg, IL, USA
Allbond 2 primer A	Bisco Inc.
Allbond 2 primer B	Bisco Inc.
Prime & Bond NT	Dentsply DeTrey GmbH, Konstanz, Germany
Transbond XT primer	3M Unitek, Monrovia, CA, USA
Vivadent Excite	Ivoclar Vivadent AG, Schaan, Lichtenstein
Optibond solo Plus	Kerr Corp., West Collins Orange, USA
Composite resins	
Allbond 2 D/C Opaquer Universal paste	Bisco Inc.
Bisfil 2B Universal Paste	Bisco Inc.
Bisfil 2B Catalyst	Bisco Inc.
Photac Fil Quick	Espe, Seefeld, Germany
Ketac Fil	Espe
Transbond XT adhesive paste	3M Unitek
Tetric Ceram	Ivoclar Vivadent AG
Tetric flow	Ivoclar Vivadent AG
Glass ionomers	
Vitrebond liner/base and glass ionomer	3M Dental Products, St. Paul, MN, USA
Dyract AP	Dentsply DeTrey GmbH

(2 min) was increased at 10°C/min to –270°C, where it was held for 15 min. The MS detector was operated at 70 eV in the electron impact mode (EI). A mass range of m/z 30–600 was used in the scan mode and the MS source temperature was 230°C. The methacrylates were identified by comparing their mass spectra to mass spectra in the Wiley library and to mass spectra reported in earlier studies (5, 6).

The target compounds were quantified by liquid chromatography (LC, Agilent 1100) with the diode array detection (HP 1040A) at 210 nm. Separation took place on a Waters Spherisorb S5 ODS2 column (250 mm, 4.6 mm ID) in the reversed phase mode by using 0.8 ml/min of acetonitrile water as mobile phase. The acetonitrile content varied from 15% (0–2 min) to 95% (30 min). The injection volume was 10 µl. The methacrylates were quantified by the external standard method. The following commercially available standards were used: 2-HEMA, hydroxypropyl methacrylate, ethyl methacrylate (EMA), ethyleneglycol dimethacrylate (EGDMA), TEGDMA, urethane dimethacrylate (UEDMA), 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]- propane (bis-GMA) and 2,2-bis(methacryloxyethoxyphenyl)propane (bis-EMA). The LC purities were over 90%. Other identified aliphatic di- and trimethacrylates were quantified by LC using the response of TEGDMA. The detection limits were 0.02–0.05% (0.5–1 µg/ml; signal to noise 3 : 1).

Results

The concentrations of identified methacrylates are summarized in Table 2 according to their occurrence in dental restorative materials. The most frequently occurring methacrylates in bonding materials were 2-HEMA and bis-GMA. Bis-GMA and TEGDMA were the most frequently occurring methacrylates in composite resins. The main methacrylate of the 2 glass ionomers was 2-HEMA or trimethylolpropane trimethacrylate. Most methacrylates could be identified by both MS and LC retention times (Figs 1 and 2). The non-volatile bis-GMA and UEDMA could only be detected by LC. In the LC method, methacrylic acid eluted at about the same time as 2-HEMA, and the small amounts identified by GC-MS could therefore not be detected and quantified by the LC method. 2 of the composite resins in the form of capsules contained no detectable acrylates or methacrylates.

Discussion

2 different chromatographic methods were used to analyse the methacrylates in dental restorative materials in order to ensure the reliability of the determinations. With the GC-MS method, volatile and semivolatile methacrylates could be detected and identified, although most methacrylates showed no molecular ions in the used EI mode, which may influence the reliability of the identification (6). For example, diethyleneglycol dimethacrylate has a similar mass spectrum to TEGDMA. Its retention time can then be used to confirm the identity, as it elutes between EGDMA and TEGDMA in the gas chromatogram. Some acrylic compounds like the non-volatile UEDMA may decompose into 2-HEMA and other degradation products at the used injector temperature,

Table 2. Concentrations of methacrylates identified in dental restorative materials

	Concentration (%, w/w)			
Identified methacrylates	Range	Median	*n*/*x**	Identification
7 bonding materials				
2-HEMA	0.3–28	17	5/2	GC-MS/LC
Bis-GMA	21–40	27	4/2	LC
EGDMA	<0.05–0.4	<0.3	4/0	GC-MS/LC
TEGDMA	4–46		2/0	GC-MS/LC
UEDMA	2–29		2/0	LC
DEGDMA	<0.05–5		2/0	GC-MS/LC
TMPTMA	3–7		2/0	GC-MS/LC
EMA	1		2/0	GC-MS/LC
Glycerin dimethacrylate	4–8		2/1	GC-MS/LC
Methacrylic acid	Not quantified		2	GC-MS
HPMA	0.3		1	GC-MS/LC
1-chloromethyl-2-hydroxyethyl methacrylate	Not quantified		1	GC-MS
8 composite resins				
Bis-GMA	6–21	10	6/6	LC
TEGDMA	3–7	6	5/4	GC-MS/LC
EGDMA	<0.05–5		4/0	GC-MS/LC
UEDMA	8–15	11	3/2	LC
Bis-EMA	6–8		2/2	GC-MS/LC
Decamethylene dimethacrylate	<0.05–1		2/0	GC-MS
2-HEMA	7		1/0	GC-MS/LC
2-(Dimethylamino)ethylmethacrylate	2		1/0	GC-MS
Bis-MA	5		1/0	GC-MS/LC
DEGDMA	Not quantified		1	GC-MS
Methacrylic acid	Not quantified		1	GC-MS
2 glass ionomers				
2-HEMA	0.2–23		2/1	GC-MS/LC
EGDMA	0.1–0.2		2	GC-MS/LC
Methacrylic acid	Not quantified		2	GC-MS
TMPTMA	9		1/0	GC-MS/LC
HPMA	0.3		1	GC-MS/LC

2-HEMA, 2-hydroxyethyl methacrylate; bis-EMA, 2,2-bis(methacryloxyethoxyphenyl)propane; bis-GMA, 2,2-bis-[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane; EGDMA, ethyleneglycol dimethacrylate; GC-MS, gas chromatography mass selective; HPMA, hydroxypropyl methacrylate; LC, liquid chromatography; TEGDMA, triethyleneglycol dimethacrylate; TMPTMA, trimethylolpropane trimethacrylate; UEDMA, urethane dimethacrylate; bis-MA, 2,2-(bis (4-methacryloxy) phenyl) propane.
**n* = number of products, where the identified methacrylate was found; *x* = number of products, where the identified methacrylate was declared in the safety data sheet.

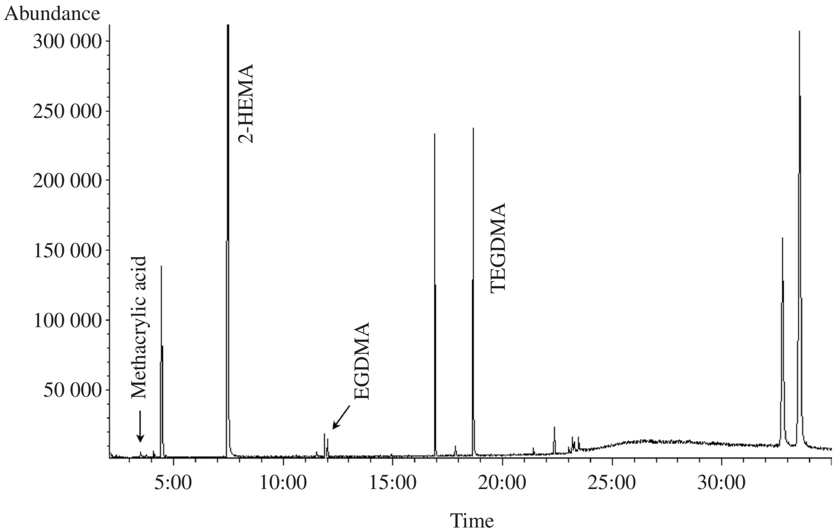

Fig. 1. Gas chromatogram of an adhesive resin (the same product as in Fig. 2). 2-HEMA, 2-hydroxyethyl methacrylate; EGDMA, ethyleneglycol dimethacrylate; TEGDMA, triethyleneglycol dimethacrylate.

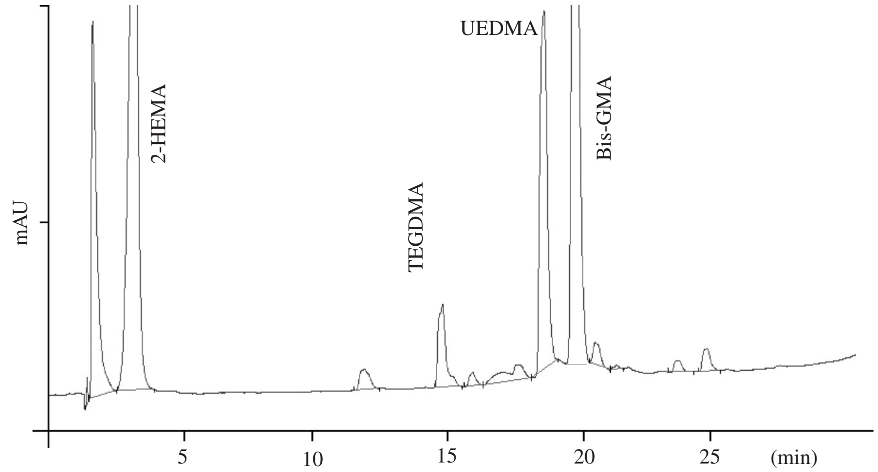

Fig. 2. Liquid chromatogram of an adhesive resin (the same product as in Fig. 1). 2-HEMA, 2-hydroxyethyl methacrylate; bis-GMA, 2,2-bis-[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane; TEGDMA, triethyleneglycol dimethacrylate; UEDMA, urethane dimethacrylate. Y-scale: −10–100 m AU.

and therefore, all methacrylates in concentrations over 2% were quantified by LC and not by GC. With this measurement strategy, most of the identifications by GC-MS were confirmed by the results of the LC method. Despite the use of 2 different methods, sodium tolylglycine glycidylmethacrylate, trimethoxysilylpropanol methacrylate and biphenyl dimethacrylate could not be detected. According to the SDS, these compounds were ingredients of a few products. Sodium tolylglycine glycidylmethacrylate was probably not soluble in the extraction medium acetone, or it was not present as such anymore due to the reactive glycidyl group. Trimethoxysilylpropanol methacrylate may also have reacted with other ingredients during extraction or analysis. Biphenyl dimethacrylate was expected to elute during the applied chromatographic conditions, but no compound that matched the chemical structure was detected.

According to this study, the semivolatile 2-HEMA was the most frequently used additive to enable the dentin bonding of the resin. Information in SDSs about 2-HEMA was given for 2 bonding materials of 5. 2-HEMA is a sensitizer and therefore its content should be given in the SDS or in the product information sheet so that dental personnels are aware of the risks and are able to choose substitutive materials. Other frequently occurring methacrylates in concentrations over 1% were bis-GMA, UEDMA and TEGDMA, which are all potential sensitizers. Information about bis-GMA was given for 2 bonding materials of 4. The contents of UEDMA and TEGDMA in bonding materials were not declared.

The bis-GMA content in composite resins was declared for all 6 products that contained bis-GMA. For TEGDMA, the situation was almost as good; 4 composite resins of 5 contained information about the TEGDMA content. The composite resin that contained 2-HEMA had no information about it.

At the time of this study, methacrylates classified as skin sensitizers present at a concentration of 1% or more in chemical preparations, such as dental materials, must be listed in SDSs based on their classification. Since August 2002, in the EU, for all chemicals that are classified as skin sensitizers, the concentration limit for providing information about the possible sensitizing effect has been 0.1% (1999/45/EU). In the case that the concentration limit for a particular chemical is mentioned in Annex I of Directive 67/548/EEC, the chemical must be declared accordingly. Methacrylates not specifically classified as sensitizers in Annex I of Directive 67/548/EEC are considered to be only irritant chemicals and must be declared in SDSs when the concentration is $\geq$1%.

To summarize the results of this study, the information about the contents of sensitizing methacrylates in the SDSs needs to be improved so that the health risks for dental personnel can reliably be assessed in order to decrease the exposure to these compounds.

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